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COMPLETE SPECIFICATION

New Printing process for Cellulosic Textile Materials

We, FREDERICK RICHARD ALSBERG, a subject of the Queen of Great Britain and a resident of Hexagon House, Blackley, Manchester and IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to a new printing process and more particularly it relates to a new printing process for cellulosic textile materials impregnated with azoic coupling components derived from 2:3-hydroxynaphthoic acid.

It is well known that cellulosic textile materials may be coloured locally by impregnating the whole of the textile material with an azoic coupling component usually from a solution in aqueous alkali, then applying locally a thickened printing paste containing a diazotised aromatic primary amine, thus forming an azo dyestuff *in situ* and subsequently washing the textile material to remove the alkali and the residual unreacted azoic coupling component. It is also well known that other classes of dyestuffs for example chrome mordant dyestuffs, vat dyestuffs, solubilised vat dyestuff, dyestuffs containing quaternary ammonium groups, basic dyestuffs or resin bonded pigment printing compositions may also be applied to the impregnated cellulosic textile material side-by-side with the diazotised aromatic primary amine in order to obtain on the same material colourations not readily obtainable from diazotised aromatic primary amines, that is to say, deep yellows, greens and blues, and, pale pinks and oranges having good fastness to light and to washing.

In United Kingdom Specifications Nos. 797,946, 798,121, 819,585 (11804/56),

838,336 (11805/56), 816,925 (13515/56),
838,338 (18560/55), 824,121 (18562/56),
821,120 (18563/56) and 820,470 (13028/57)

there are described processes, including printing processes, for the colouration of cellulosic textile materials with water-soluble dyestuffs having s-triazinylamino groups which contain one or more halogen atoms attached to carbon atoms of the triazine nucleus, which comprise applying one of the said dyestuffs in aqueous medium in conjunction with a treatment with an acid-binding agent.

In the said specifications there are mentioned, as examples of acid-binding agents which may be used, the alkali metal salts of weak acids.

When the printing processes described in the said specifications are applied to cellulosic textile materials which have previously been impregnated with a caustic alkali and an azoic coupling component derived from 2:3-hydroxynaphthoic acid, weak prints are obtained, whether or not acid-binding agents, as described in the said specifications, are added to the print paste or applied in a prior- or an after-treatment.

It has now been found, however, that when the printing paste used in a printing process described in the said specifications is one containing a dihalogeno-s-triazinyl-amino group much stronger prints can be obtained on cellulosic textile materials impregnated as aforesaid, by the addition of alkali metal salts of sulphurous acid to the printing paste.

According to the present invention, therefore, there is provided a printing process for cellulosic textile materials which comprises impregnating the textile material with an alkali and an azoic coupling component derived from 2:3-hydroxynaphthoic acids, applying one thickened printing paste containing a diazotised aromatic primary amine and a different thickened printing paste containing an alkali metal salt of a sulphurous acid.

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acid and a water-soluble dyestuff containing a dihalogeno-*s*-triazinyl-amino group and thereafter heating or steaming the printed textile material.

5 The cellulosic textile material may be impregnated, for example, by padding through a solution of azoic coupling component derived from 2:3-hydroxynaphthoic acid, for example 2-hydroxy-3-naphthoic anilide, in dilute aqueous alkali, and then drying the treated textile material.

The printing pastes used in the process may be thickened with any of the usual thickening agents, for example starch, gum tragacanth, locust bean gum, emulsified hydrocarbon oils or sodium alginate. They may also contain other commonly used adjuvants for printing pastes, for example, urea, glycerine or thioglycol.

15 As examples of diazotised aromatic primary amines present in the first-mentioned printing paste there may be mentioned the diazo compounds from *o*-nitroaniline, 2:5-dichloroaniline, 4'-nitro-4-amino-2:5-dimethoxyazobenzene or from 3:3'-dimethoxy-4:4'-diaminoazobenzene.

The dyestuffs contained in the other type of printing paste used in the process may be obtained from colouring matters, of for example the azo and anthraquinone series, containing such solubilising groups as, for example, sulphonic acid or carboxylic acid groups, and also containing amino or mono-substituted amino groups, by interaction of the said colouring matters with a cyanuric halide, for example cyanuric chloride. Suitable dyestuffs are described, for example, in United Kingdom Specifications Nos. 209,723, 298,494, 772,030, 774,125, 781,930, 785,120, 40 785,222 and 33809/55, 826,405.

45 As examples of alkali metal salts of sulphurous acid which may be used in the process of the invention there may be mentioned sodium sulphite, potassium metabisulphite and sodium bisulphite.

The two printing pastes may be applied in either order, and the textile material may, if desired, be dried between each printing step. The printing pastes may be applied by any of 50 the commonly used methods, for example by roller, screen, or hand block.

The printed textile material is then preferably dried, for example by passing through a drying chamber at a temperature of 50° C. to 80° C., and then the dyestuffs are fixed on the fibre by steaming or heating the textile material at a temperature of 95° C. to 120° C. for a short period of time for example for 5 minutes or less.

55 60 The textile material is then scoured, for example by treatment in a boiling dilute aqueous solution of soap or detergent.

The new process is valuable for the printing of cellulosic fabrics, especially cotton,

since it allows the production, by a simple process, of a wide range of colourations not hitherto readily obtainable by printing with other classes of dyestuff alongside azo dyestuffs formed *in situ* on the fabric.

The invention is illustrative but not limited by the following examples in which parts and percentages are by weight:

EXAMPLE 1.

Cotton fabric is padded with a 2% solution of 2-hydroxy-3-naphthoic anilide in 0.8% aqueous caustic soda solution. The following printing pastes are then applied by rollers:

PRINTING PASTE (1).

	Parts
Dyestuff described in Example 1 of U.K. Specification No. 797,946	80
Urea	3
Water	53
Sodium alginate (5% aqueous solution)	85
Potassium sulphite liquor (specific gravity 1.45)	40
	1.5

PRINTING PASTE (2).

	Parts
Stabilised diazo salt of 4-benzamido-2:5-diethoxyaniline	90
Water	2
Starch tragacanth	36
40% aqueous acetic acid solution	60
	95

The fabric is dried, steamed for 2 minutes, rinsed in water, "soaped" by boiling for 5 minutes in an aqueous solution containing 0.2% of sodium carbonate and 0.3% of a condensate of ethylene oxide with an alkyl phenol, and then finally dried.

A red and navy-blue print is obtained where the red shade is much stronger than one obtained from a printing paste from which potassium sulphite has been omitted.

100

105

EXAMPLE 2.

A mercerised cotton fabric is padded with a 2% solution of 2-hydroxy-3-naphthoic anilide in 0.8% aqueous caustic soda solution. The following printing pastes are applied by screen-printing:

PRINTING PASTE (1).

	Parts
Dyestuff described in Example 2 of U.K. Specification No. 797,946	115
Urea	3
Water	5
Sodium alginate (5% aqueous solution)	51
Sodium bisulphite (40% aqueous solution)	40
	120
	1.25

PRINTING PASTE (2).

		Parts
5	Stabilized diazo salt of 2:5-dichloroaniline	4
5	Water	34
	Starch tragacanth	60
13	40% aqueous acetic acid	2
	The print is dried, heated on drying cylinders for 30 seconds to 1 minute at 105°C., and rinsed and "soaped" as described in Example 1.	

A yellow and red printed design is obtained where the yellow is stronger than one obtained from a printing paste from which the sodium bisulphite has been omitted.

If in the above example the dyestuff used in printing paste No. 1 is replaced by the dyestuff described in Example 5 of United Kingdom specification No. 798,121 a blue and red printed design is obtained where the blue is stronger than one from a printing paste from which the sodium bisulphite has been omitted.

EXAMPLE 3.

25 A cotton fabric is padded with a 2% solution of 2-hydroxy-3-naphthoic-2'-methoxy-anilide in 0.8% aqueous caustic soda solution. The following printing pastes are applied by roller:—

PRINTING PASTE (1).

		Parts
30	Dyestuff of Example 4 of United Kingdom Specification No. 774,925	5
35	Urea	10
	5% sodium alginate solution	50
	Water	34
	40% sodium bisulphite solution	1.25

PRINTING PASTE (2).

40	Stabilised diazo salt of 6-benzamido-4-methoxy-3-amino-toluene	1
	Water	37
	Starch tragacanth	60
	40% aqueous acetic acid	2

45 The fabric is dried, steamed for 5 minutes, then rinsed and "soaped" as described in Example 1.

A yellow and violet printed design is obtained in which the yellow is stronger than one obtained from a printing paste from

which the sodium bisulphite has been omitted.

If in the above example, the dyestuff in printing paste No. 1 is replaced by 5 parts of a 4:1 mixture of the dyestuff of Example 4 of United Kingdom Specification 33809/55 No. 826,405 and the dyestuff of Example 1 of the United Kingdom Specification No. 781,930, and the diazo salt of 6-benzamido-4-methoxy-3-amino-toluene in printing paste No. 2 is replaced by 3 parts of a diazo salt of *m*-chloroaniline, there is obtained a green and orange printed design in which the green is much stronger than if the sodium bisulphite had been omitted.

Similarly, by applying one printing paste made up as No. 1 above but containing 2% of the dyestuff of Example 1 of United Kingdom Specification No. 33809/55 (Serial No. 826,405), a second printing paste made up as No. 1 above but containing 2% of disodium 1-amino-4-(3'-dichlorotriazinylaminoanilino) anthraquinone-4'-disulphonate and a third printing paste made up as No. 2 above but containing 1.5% of the diazo salt of 3-nitro-4-aminoanisole, there is obtained a yellow, blue and bordeaux printed design.

If there is used $\frac{1}{2}$ % of disodium 2-N-(dichlorotriazinyl)-N-methylamino-7-(4'-methoxyphenylazo)-8-naphthol-2'-6-disulphonate as the dyestuff in printing paste No. 1 and 4% of a diazo salt of 4'-nitro-4-amino-2:5-dimethoxyazobenzene in printing paste No. 2, there is obtained a pale pink and black printed design.

WHAT WE CLAIM IS:—

(1) Printing process for cellulosic textile materials which comprises impregnating the textile material with an alkali and an azoic coupling component derived from 2:3-hydroxynaphthoic acid, applying one thickened printing paste containing a diazotised aromatic primary amine and a different thickened printing paste containing an alkali metal salt of sulphurous acid and a water-soluble dyestuff containing a dihalogeno-*s*-triazinylamino group and thereafter heating or steaming the printed textile material.

(2) Printing process for cellulosic textile materials as hereinbefore particularly described especially with reference to the foregoing examples.

WALTER SCOTT,
Agent for the Applicants.

PROVISIONAL SPECIFICATION New Printing process for Cellulosic Textile Materials

We, FREDERICK RICHARD ALSBERG, a subject of the Queen of Great Britain and a resident of Hexagon House, Blackley, Manchester and IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British company, do

hereby declare this invention to be described in the following statement:—

This invention relates to a new printing process and more particularly it relates to a new printing process for cellulosic textile materials impregnated with azoic coupling

components derived from 2:3-hydroxynaphthoic acid.

It is well known that cellulosic textile materials may be coloured locally by impregnating the whole of the textile material with an azoic coupling component usually from a solution in aqueous alkali, then applying locally a thickened printing paste containing a diazotised aromatic primary amine, and subsequently washing the textile material to remove the alkali and the residual unreacted azoic coupling component. It is also well known that other classes of dyestuffs for example chrome mordant dyestuffs, vat dyestuffs, solubilised vat dyestuffs, dyestuffs containing quaternary ammonium group, basic dyestuffs or resin bonded pigment printing compositions may also be applied to the impregnated cellulosic textile material side-

5 by-side with the diazotised aromatic primary amine in order to obtain on the same material colourations not readily obtainable from diazotised aromatic primary amines.

10 In United Kingdom Specifications Nos. 797,946 (34503/54), 798,121 (34504/54) 25 7955/56 (Serial No. 805,562), 18560/56, 824,121 (18562/56 and 821,120 (18563/56) there are described processes, including printing processes, for the colouration of cellulosic 30 textile materials with water-soluble dyestuffs having nitrogen-containing heterocyclic groups, which heterocyclic groups contain halogen atoms in ortho and/or para position to the nitrogen atoms of heterocyclic nuclei, 35 which comprises applying one of the said dyestuffs in aqueous medium in conjunction with a treatment with an acid-binding agent.

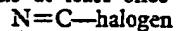
In the said specifications there are mentioned, as examples of acid-binding agents 40 which may be used, the alkali metal salts of weak acids.

When the printing processes described in the said specifications are applied to cellulosic textile materials which have previously been 45 impregnated with a caustic alkali and an azoic coupling component derived from 2:3-hydroxynaphthoic acid, weak prints are obtained, whether or not acid-binding agents, as described in the said specifications, are added to the print paste or applied in a prior- or an after-treatment.

It has now been found, however, that when alkali metal salts of sulphurous acid are added to the printing paste used in the printing processes described in the said specifications 55 much stronger prints are obtained on cellulosic textile materials impregnated as aforesaid, than are obtained in the absence of alkali metal salts of sulphurous acid.

According to the present invention, therefore, there is provided a printing process for cellulosic textile materials which comprises impregnating the textile material with an alkali and an azoic coupling component 60 derived from 2:3-hydroxynaphthoic acid,

applying one thickened printing paste containing a diazotised aromatic primary amine and a different thickened printing paste containing an alkali metal salt of sulphurous acid and a dyestuff containing a heterocyclic ring which contains at least once the group:—



and thereafter heating or steaming the printed textile material.

The cellulosic textile material may be impregnated, for example, by padding through a solution of azoic coupling component derived from 2:3-hydroxynaphthoic acid, for example, 2:3-hydroxynaphthoic acid, for example 2-hydroxy-3-naphthoic anilide, in dilute aqueous alkali, and then drying the treated textile material.

The printing pastes used in the process may be thickened with any of the usual thickening agents, for example starch, gum tragacanth, locust bean gum or sodium alginate. They may also contain other commonly used adjuvants for printing pastes, for example urea, glycerine or thioglycol.

As examples of diazotised aromatic primary amines present in the first-mentioned printing paste there may be mentioned the diazo compounds from *o*-nitraniline, 2:5-dichloraniline, 4'-nitro-4-amino-2:5-dimethoxyazobenzene or from 3:3'-dimethoxy-4:4'-diaminazobenzene.

The dyestuffs contained in the other printing paste used in the process may be obtained from colouring matters, of for example the azo and anthraquinone series, containing ionogenic solubilising groups for example sulphonate acid or carboxylic acid groups, and also containing amino or mono-substituted amino groups, by interaction of the said colouring matters with a heterocyclic compound, for example cyanuric chloride or 2:4:6-trichloropyrimidine, containing at least twice the grouping of the formula $\text{---N}=\text{C}-\text{halogen}$.

Where two or more such groupings are still present in the dyestuff molecule, the product may be further reacted with, for example, the same or a different colouring matter as hereinbefore defined, or with a colourless compound containing a group having a reactive hydrogen atom, for example an amine, a mercaptan, a phenol or an alcohol, always provided that at least one grouping of the said formula is still present in the final dyestuff. Suitable dyestuffs are described, for example, in the aforesaid specifications.

As examples of alkali metal salts of sulphurous acid which may be used in the process of the invention there may be mentioned sodium sulphite, potassium metabisulphite and sodium bisulphite.

The two printing pastes may be applied in either order, and the textile material may, if desired, be dried between each printing

step. The printing pastes may be applied by any of the commonly used methods, for example by roller, screen, or hand block.

5 The printed textile material is then preferably dried, for example, by passing through a drying chamber at a temperature of 50° C. to 80° C., and then the dyestuffs are fixed on the fibre by steaming or heating the textile material at a temperature of 95° C. to 120° C. for a short period of time for example for 5 minutes or less.

10 The textile material is then scoured, for example by treatment in a boiling dilute aqueous solution of soap or detergent.

15 The invention is illustrated but not limited by the following examples in which parts and percentages are by weight:—

EXAMPLE 1.

20 Cotton fabric is padded with a 2% solution of 2-hydroxy-3-naphthoic anilide in 0.8% aqueous caustic soda solution. The following printing pastes are then applied by rollers:—

PRINTING PASTE (1).

	Parts
25 Dyestuff described in Example 1 of U.K. Specification No. 34503/54 (797,946)	3
Urea	3
Water	53
30 Sodium alginate (5% aqueous solution)	40
Potassium sulphite liquor (specific gravity 1.45)	1.5

PRINTING PASTE (2).

	Parts
35 Stabilised diazo salt of 4-benzamido-2:5-diethoxyaniline	2
Water	36
Starch tragacanth	60
40 40% aqueous acetic acid solution	2
45 The fabric is dried, steamed for 2 minutes, rinsed in water, "soaped" by boiling for 5 minutes in an aqueous solution containing 0.2% of sodium carbonate and 0.3% of a condensate of ethylene oxide with an alkyl phenol, and then finally dried.	The print is dried, heated on drying cylinders for 30 seconds to 1 minute at 105° C., and rinsed and "soaped" as described in Example 1.

A red and navy-blue print is obtained where the red shade is much stronger than one obtained from a printing paste from which potassium sulphite has been omitted. 50

EXAMPLE 2.

A mercerised cotton fabric is padded with a 2% solution of 2-hydroxy-3-naphthoic anilide in 0.8% aqueous caustic soda solution. The following printing pastes are applied by 55 screen-printing:—

PRINTING PASTE (1).

	Parts
Dyestuff described in Example 2 of U.K. Specification No. 34503/54 (797,946)	60
Urea	3
Water	5
Sodium alginate (5% aqueous solution)	51
Sodium bisulphite (40% aqueous solution)	40 65
	1.25

PRINTING PASTE (2).

	Parts
Stabilised diazo salt of 2:5-dichloroaniline	70
Water	4
Starch tragacanth	34
40% aqueous acetic acid	60
The print is dried, heated on drying cylinders for 30 seconds to 1 minute at 105° C., and rinsed and "soaped" as described in Example 1.	75
A yellow and red printed design is obtained where the yellow is stronger than one obtained from a printing paste from which the sodium bisulphite has been omitted.	80
If in the above example the dyestuff used in printing paste No. 1 is replaced by the dyestuff described in Example 5 of United Kingdom Specification No. 34504/54 (Serial No. 798,121) a blue and red printed design is obtained where the blue is stronger than one from a printing paste from which the sodium bisulphite has been omitted.	85
WALTER SCOTT, Agent for the Applicants.	90

